Summary

Because of the general immiscibility of homopolymers and the connectivity between chemically different chains, block copolymers spontaneously form ordered nanometer-sized structures. In diblock copolymer systems the variety of structures is rather limited, since only the molecular weight and one block fraction can be chosen freely as design parameters. Inclusion of additional building blocks (e.g. linear triblock terpolymers) usually gives rise to more complex phase behavior and also enables design of more complex architectures, like star-shaped and multiblock copolymers.

Preparation of such well-defined macromolecules is, however, a very challenging task, as usually multiple steps and inert reaction conditions are required. Furthermore, successful synthesis does not automatically imply the material to self-assemble into an ordered morphology. By combining simple diblock copolymers and supramolecular chemistry, both complex synthesis routes and the reduced mobility of high molecular weight multiblock copolymers can be avoided. Comb-shaped copolymers based on hydrogen bonded poly(4-vinylpyridine) (P4VP) and alkylphenol surface active molecules, 3-pentadecylphenol (3-PDP) and 4-nonadecylphenol (4-NDP) in particular, have been studied extensively during the past decades. Proper balance between attractive and repulsive forces caused such supramolecular complexes to form a layered glassy polymer/crystalline amphiphilic structure at room temperature. A unique property of this specific system is that on heating, before entering the disordered state, melting of the alkylphenol side chains first results in a liquid crystalline lamellar morphology. When extended from P4VP homopolymers to polystyrene-containing (PS) diblock copolymers, often hierarchical structures (i.e. structures within another structure) are obtained because of simultaneous microphase separation of the diblock copolymer and the comb copolymer.

The work described in this thesis is focused on further development of these supramolecular block copolymer-based systems, with special attention given to so-called double-comb diblock copolymers. Instead of combining P4VP ho-

mopolymers or P4VP-*b*-PS diblock copolymers with alkylphenol surfactants, P4VP-based diblock copolymers containing a second block capable of accepting hydrogen bonds are used for the preparation of such comb-comb diblock copolymers. Unusual phase behavior was expected to arise in this new class of supramolecular materials.

Chapter 1 gives an overview of the most recent advances in block copolymer science, providing several examples of both self-assembling covalent- and supramolecular-based block copolymers. In addition, the most important characterization techniques specific for studying bulk phase behavior are introduced, including small-angle X-ray Scattering (SAXS) and transmission electron microscopy (TEM). Finally, the synthesis of block copolymers is addressed briefly.

Whereas both P4VP(3-PDP)$_{1.0}$ and P4VP(4-NDP)$_{1.0}$ were previously found to self-assemble into layered structures, their thermal properties were found to be rather different. The longer alkyl tail of 4-NDP indeed caused the complex to melt at a higher temperature, but compared to 3-PDP the order-disorder transition temperature (T_{ODT}) increased with almost 30 °C to 97 °C. Since the synthesis route presented in Chapter 2 enables synthesis of any alkylphenol possible, additional alkylphenol surfactants were prepared and complexed to P4VP. By systematic variation of the tail length (from 13 up to 21 methylene units) and the hydroxyl position (ortho, meta and para), several interesting observations were made in the stoichiometric (i.e. $x = 1.0$) supramolecular P4VP(n-alkylphenol)$_x$ comb copolymers. As expected, both the melting point and size of the lamellar structure increased with tail length. Surprisingly though and independent of the tail length, T_{ODT} remained constant in the meta- and para-substituted complexes, while microphase separation in the ortho-substituted complexes was found to be crystallization driven. Since the strength of hydrogen bonding is unaffected by the hydroxyl position, the different phase behavior had to be caused by a purely steric effect. For this reason, the highest order-disorder transition was discovered in the sterically least hindered para complexes.

The hygroscopic nature of poly(*N*,*N*-dimethylacrylamide) (PDMA) in our first [P4VP-*b*-PDMA](3-PDP)$_x$ supramolecular double-comb diblock copolymer caused analysis of this complex to be rather challenging. For this reason, it was replaced by another acrylamide-based block: poly(*N*-acryloylpiperidine) (PAPI). Chapter 3 describes the synthesis and self-assembly of pristine P4VP-*b*-PAPI diblock copolymers in detail. Several diblocks with varying molecular weight and composition were prepared by reversible addition-fragmentation

chain transfer (RAFT) polymerization. Microphase separation of these copolymers resulted in numerous of the classical morphologies, including spheres, cylinders and lamellae. Furthermore, an approximation for the Flory-Huggins interaction parameter was obtained via a random copolymer blend approach. Its value ($\chi_{4VP,API} \approx 0.03$) was found to be in excellent agreement with phase behavior observed in symmetric, low molecular weight analogues.

A double perpendicular lamellar-*in*-lamellar morphology was observed in [P4VP-*b*-PDMA](3-PDP)$_{1.0}$ before, although according to previously developed theoretical models additional structures could be formed in double-comb diblock copolymers by adjusting the molecular weight, composition or grafting density. Enhanced self-assembly of a symmetric ($f_{P4VP} \approx 0.5$) [P4VP-*b*-PAPI](3-NDP)$_x$ supramolecular double-comb diblock copolymer is demonstrated in Chapter 4. Self-assembly of the high comb density complex ($x = 1.0$) led to a double perpendicular lamellar-*in*-lamellar structure, whereas the predicted, more stable parallel orientation of the internal structure was observed in the $x = 0.5$ complex. Using the same symmetric P4VP-*b*-PAPI diblock copolymer, the preference of 3-NDP for the acrylamide block became visible on further lowering the concentration of 3-NDP to $x = 0.3$, leading to spontaneous formation of cylinders-*in*-lamellae. Further dilution to $x = 0.1$ only allowed 3-NDP to plasticize the copolymer, resulting in highly ordered large lamellae, but lacking the presence of an internal structure. Thus, multiple unique hierarchical structures were discovered in [P4VP-*b*-PAPI](3-NDP)$_x$ supramolecular double-comb diblock copolymers by using a single P4VP-*b*-PAPI copolymer and simply adjusting the side chain density.

Chapter 5 deals with a more detailed analysis of the two most interesting double-comb structures: the double perpendicular ($x = 1.0$) and double parallel ($x = 0.5$) alignment of the internal lamellae. For this study the comb density x was kept constant, while the molecular weight of the symmetric, lamella-forming diblock copolymer was varied. Temperature-resolved SAXS demonstrated that, although all highly diluted $x = 1.0$ complexes formed a disordered melt at high temperatures, sequential crystallization of 3-NDP in both comb blocks still enabled formation of double perpendicular lamellae. Furthermore, the liquid crystalline P4VP(3-NDP) block facilitated both thermal treatment and orientation. The $x = 0.5$ complexes on the other hand showed an increase of the number of internal layers with molecular weight. Formation of multiple small lamellae instead of a single amphiphilic layer was thought to be entropically favorable, whereas the fixed small feature size was attributed to the preferential interdigitated orientation of 3-NDP's aliphatic tails. The observed scaling be-

havior of the number of internal lamellae with molecular weight enables design of multiblock-like structures with great precision.

The combination of 3-NDP and asymmetric cylinder- or sphere-forming P4VP-*b*-PAPI diblock copolymers is presented in the last chapter (Chapter 6), as hypothetically rather interesting morphologies could appear in such complexes. However, their crystalline nature and the tendency of these bottlebrush-like block copolymers to form a flat interface caused the high grafting density complexes ($x = 0.5 - 1.0$) to form fairly undefined large length scale structures. Lower comb densities ($x = 0.1 - 0.3$) resulted in most double-combs to behave like comb-coil diblock copolymers due to the amphiphiles being preferably solubilized in the PAPI phase, thereby only allowing the formation of a small structure within this acrylamide block. To conclude, the observed phase behavior was found to be strongly related to self-assembly of semicrystalline block copolymers: in general, high values of x resulted in a breakout crystallization mechanism, while confined crystallization within a large, vitrified block copolymer structure was observed for lower 3-NDP concentrations.